

Electronic Excited States in Extreme Limits via Ensemble Density Functionals

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Density functional theory (DFT) has greatly expanded our ability to affordably compute and understand electronic ground states, by replacing intractable *ab initio* calculations by models based on paradigmatic physics from high- and low-density limits. But, a comparable treatment of excited states lags behind. Here, we solve this outstanding problem by employing a generalization of density functional theory to ensemble states (EDFT). We thus address important paradigmatic cases of all electronic systems in strongly (low-density) and weakly (high-density) correlated regimes. We show that the high-density limit connects to recent, exactly solvable EDFT results. The low-density limit reveals an unnoticed and most unexpected result—density functionals for strictly correlated *ground* states can be reused *directly* for excited states. Nontrivial dependence on excitation structure only shows up at third leading order. Overall, our results provide foundations for effective models of excited states that interpolate between exact low- and high-density limits, which we illustrate on the cases of singlet-singlet excitations in H_2 and a ring of quantum wells.

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Preamble.—Density functional theory (DFT) [1,2] is best known as a computational modeling tool used in tens of thousands of *applicative* scientific papers every year. What is less widely known is that DFT offers a natural connection between quantum mechanics and paradigmatic physical conditions (high- and low-density limits) of matter, in which electronic correlations attain two quantitatively (weak and strong, respectively) and qualitatively different fundamental ends. In this context, DFT serves as a formal tool to understand the behavior of ground state electronic structure via a rigorous constrained variational approach to the electronic structure problem. Understanding of paradigmatic conditions then informs model development, e.g., the popular “PBE” [3] approximation, and computational studies therefrom.

Unfortunately, DFT is only defined for ground states, so cannot elucidate the structure of excited states. This Letter will demonstrate that *ensemble* density functional theory (EDFT) for excited states [4,5] can tackle this outstanding problem. We shall show that recently derived Hartree and exchange physics [6,7] become exact in the high density (weak interaction) limit; so high-density excited electronic

states may be solved using these tools. More importantly, we shall show that the *low density (strong interaction) limit of excited states behaves exactly like a ground state*. Therefore, the full suite of *ground state* strictly correlated electron (SCE) tools and approximations [8–13] may be used to solve both ground and excited states of low-density many-electron systems.

Our Letter thereby improves understanding of excited states in paradigmatic limits and connects their behavior to well-defined density functionals for which exact forms and approximations are available. It presents a crucial step toward efficient excited state approximations that capture important limits; and promises to accelerate and generalize recent progress on low cost modeling of single [14–19] and double excitations [16,20–23] that may range from weakly to strongly correlated regimes.

The rest of this Letter proceeds as follows: First, we introduce EDFT and show how it can be used to understand the high- and low-density limits of interacting electrons in realistic inhomogeneous systems. Then, using as an illustration the strong interaction limit of electrons in a harmonic well, we derive the asymptotic properties of

the density functionals for describing excitations in Wigner-like systems via EDFT. We then reveal that the *second leading* term in the low-density limit is also the same in ground and excited states, and that a nontrivial dependence only appears in the *third leading* term—which therefore describe more realistic correlated excitations. We then illustrate the importance of our findings for applications by studying excitations in two examples. Finally, we conclude.

Theoretical framework.—Excited state EDFT is concerned with the behavior of countable sets of excited states. In practice, a finite set of low-lying solutions of $\hat{H}|\kappa\rangle = E_\kappa|\kappa\rangle$. These are grouped in an ensemble state $\hat{\Gamma}^w = \sum_\kappa w_\kappa|\kappa\rangle\langle\kappa|$ using some prescribed weights [24] such that $w_\kappa \geq 0$ and $\sum_\kappa w_\kappa = 1$ (collectively, w). The average of an operator, \hat{O} , over $\hat{\Gamma}^w$ is given by $\mathcal{O}^w := \text{Tr}[\hat{\Gamma}^w \hat{O}]$. Crucially, choosing $w_\kappa \leq w_{\kappa'}$ for $E_\kappa \geq E_{\kappa'}$, ensures that $\hat{\Gamma}^w$ fulfills an extended variational principle [4] according to which $\mathcal{E}^w = \inf_{\hat{\Gamma}^w_{\text{trial}}} \text{Tr}[\hat{\Gamma}^w_{\text{trial}} \hat{H}]$ where the argument for the infimum (usually a minimum), $\hat{\Gamma}^w_{\text{trial}} = \sum_\kappa w_\kappa|\kappa_t\rangle\langle\kappa_t|$, involves prescribed weights, w , and mutually orthonormal trial wave functions $|\kappa_t\rangle$.

Density functionalizing the above variational principle in terms of the ensemble particle density, n , yields [5,6]

$$\mathcal{E}^w = \min_n \left\{ \mathcal{T}_s^w[n] + \mathcal{E}_{\text{Hxc}}^w[n] + \int n(\mathbf{r})v_{\text{ext}}(\mathbf{r})d\mathbf{r} \right\}. \quad (1)$$

Here, $\mathcal{T}_s^w[n] = \min_{\hat{\Gamma}^w_{\text{trial}} \rightarrow n} \text{Tr}[\hat{\Gamma}^w_{\text{trial}} \hat{T}]$ is the kinetic energy of the Kohn-Sham (KS) system—i.e., an auxiliary systems reproducing the particle density of the ensemble; the minimum is attained at $\hat{\Gamma}_s^w \equiv \sum_\kappa w_\kappa|\kappa_s\rangle\langle\kappa_s|$ [26]. $\mathcal{E}_{\text{Hxc}}^w[n]$ takes care of the remaining Hartree (H), exchange (x), and correlation (c) energies. Together, they yield the “universal” functional for ensembles: $\mathcal{F}^w = \mathcal{T}_s^w + \mathcal{E}_{\text{Hxc}}^w$.

In fact, Eq. (1) describes *different functionals* for every choice of w . To stress this important point we use capital calligraphic letters to refer to energies of mixed states; and superscripts, w , to indicate quantities that explicitly depend on their weights. *Pure* ground states involve setting $w_0 = 1$ ($\hat{\Gamma}^0 = |0\rangle\langle 0|$) for which Eq. (1) attains usual DFT forms. Spin and spatial symmetries are preserved at the Kohn-Sham level [27] (see high-density limit discussion for further details) by equally weighting degenerate states. Varying weights (e.g., via partial derivatives) lets us address *individual* excited states. [28] Therefore, the weight dependence of ensemble functionals is directly related to the structure and behavior of ground and excited electronic states.

The universal energy functional may be generalized to

$$\mathcal{F}^{\lambda,w}[n] = \inf_{\hat{\Gamma}^w \rightarrow n} \text{Tr}[\hat{\Gamma}^w (\hat{T} + \lambda \hat{V}_{\text{ee}})], \quad (2)$$

where \hat{T} is the kinetic energy operator and \hat{V}_{ee} is the Coulombic interaction operator. λ sets the strength of the interaction. This functional is referred to as “universal” because the external potential, which specifies the system we wish to treat, does not appear explicitly in its definition [the density being given and fixed in Eq. (2)]. Matching terms from above yields $\mathcal{F}^w \equiv \mathcal{F}^{\lambda=1,w}$, $\mathcal{T}_s^w \equiv \mathcal{F}^{0,w}$ and $\mathcal{E}_{\text{Hxc}}^w := \mathcal{F}^w - \mathcal{F}^{0,w}$. In fact, we stress that \mathcal{F} , \mathcal{T}_s and \mathcal{E}_{Hxc} are multiuniversal because each set of weights, w , defines a different excitation structure and, thus, a different universal functional. As we shall show below, this multiuniversality evolves into a *simple* universality in the low-density limit of matter.

In what follows, our main objective is to determine the salient behavior of key ensemble density functionals in the high-density (weakly interacting) and low-density (strictly interacting) limits. In doing so, we shall extend to excited states concepts and core results which have previously been worked out for pure ground states only [8–13]. These works can be understood as providing a generalization of the seminal work of Wigner [29,30] to *inhomogeneous* systems within DFT. Our current Letter completes the generalization to include *excited* inhomogeneous systems within EDFT. It thus provides a complete treatment of the electronic structure of two important paradigmatic and fundamentally different regimes, within a consistent and versatile approach.

High-density limit.—In the parlance of modern density functional theory, the high- and low-density limits entail uniform scaling of the coordinates of the electrons, say, by $\gamma > 0$ in such a way $n(\mathbf{r}) \rightarrow \gamma^3 n(\gamma\mathbf{r}) \equiv n_\gamma(\mathbf{r})$. To keep the discussion simple, we may think of a finite system like an atom, molecule, or quantum dot. Uniform scaling and the adiabatic constant integration in EDFT, were introduced by Nagy [31]. Scaling gives $\hat{T} \rightarrow \gamma^{-2} \hat{T}_\gamma$ and $\hat{V}_{\text{ee}} \rightarrow \gamma^{-1} \hat{V}_{\text{ee},\gamma}$. We find

$$\mathcal{F}^{\lambda,w}[n_\gamma] = \gamma^2 \mathcal{F}^{\lambda/\gamma,w}[n]. \quad (3)$$

Because the scaled ensemble density is the density of a stationary ensemble of the Hamiltonian with interaction $\lambda = 1/\gamma$, we see that the high- and low-density limits are related to the weak- and strong-interaction limits, respectively [32].

Let us first consider the high-density (i.e., weak interaction, $\gamma \rightarrow \infty$) limit. Scaling yields

$$\lim_{\gamma \rightarrow \infty} \frac{\mathcal{F}^w[n_\gamma]}{\gamma^2} = \mathcal{T}_s^w[n], \quad \lim_{\gamma \rightarrow \infty} \frac{\mathcal{E}_{\text{Hxc}}^w[n_\gamma]}{\gamma} = \mathcal{E}_{\text{Hxc}}^w[n], \quad (4)$$

where the second result follows from the definition [6] of \mathcal{E}_{Hxc} as a gradient of \mathcal{F} . The high-density limit thus inherits good properties of \mathcal{E}_{Hxc} [6,7,23,27]: (i) it preserves spin and spatial symmetries of the system; (ii) the relevant KS states can be linear combinations of Slater determinants (SDs)

that are eigenstates of spin and proper generators of point groups, unlike the single SD of conventional spin-DFT treatments; (iii) yet, it enables effective reuse of conventional spin-density functional approximations for exchange, via combination rules or on-top pair densities [7,17,19,23].

Next, consider the adiabatic connection formula,

$$\mathcal{E}_{\text{Hxc}}^w[n] = \mathcal{F}^w[n] - \mathcal{F}^{0,w}[n] = \int_0^1 \mathcal{V}_{\text{ee}}^{\lambda,w}[n] d\lambda, \quad (5)$$

$$\mathcal{V}_{\text{ee}}^{\lambda,w}[n] = \lim_{\eta \rightarrow 0^+} \frac{\mathcal{F}^{\lambda+\eta,w} - \mathcal{F}^{\lambda,w}}{\eta} := \text{Tr}[\hat{V}_{\text{ee}} \hat{\Gamma}^{\lambda+,w}]. \quad (6)$$

The ‘‘Hx’’ component is recovered as $\mathcal{E}_{\text{Hx}}^w[n] = \mathcal{V}_{\text{ee}}^{0,w}[n]$. Scaling gives $\mathcal{E}_{\text{Hxc}}^w[n_\gamma] = \gamma^2 \int_0^1 \mathcal{V}_{\text{ee}}^{\lambda,w}[n] d\lambda$, from which (for finite systems) we get, [33]

$$\mathcal{F}^w[n_\gamma] \xrightarrow{\gamma \rightarrow \infty} \gamma^2 \mathcal{T}_s^w[n] + \gamma \mathcal{E}_{\text{Hx}}^w[n] + \mathcal{E}_c^{\text{GL2},w}[n] + \dots \quad (7)$$

The first correlation contribution follows from Gorling-Levy [34] perturbation theory for ensembles, [35] which must also be adapted for KS states in the form of linear combinations of SDs. Correlations may alternatively be captured by employing expressions previously reported in Refs. [7,36,37]; as in, e.g., Ref. [23].

Low-density limit.—Approaching a most striking, and previously unnoticed fact, let us turn to the low-density (i.e., strong interaction, $\gamma \rightarrow 0^+$) limit,

$$\lim_{\gamma \rightarrow 0^+} \mathcal{F}^{1,w}[n_\gamma] = \lim_{\gamma \rightarrow 0^+} \mathcal{V}_{\text{ee}}^{1,w}[n_\gamma]. \quad (8)$$

Crucially,

$$\lim_{\gamma \rightarrow 0^+} \frac{\mathcal{V}_{\text{ee}}^{1,w}[n_\gamma]}{\gamma} = \mathcal{V}_{\text{ee}}^{\text{SCE},w}[n] \equiv V_{ee}^{\text{SCE}}[n] \quad (9)$$

where $V_{\text{ee}}^{\text{SCE}}[n] = \inf_{\Psi \rightarrow n} \langle \Psi | \hat{V}_{\text{ee}} | \Psi \rangle$ is the known interaction energy functional of strictly correlated electrons in a *ground state*, but here evaluated at the ensemble particle density. This result says that, in the low-density limit, the functional dependence on weights disappears from both $\mathcal{F}^{1,w}[n_\gamma]$ and $\mathcal{V}_{\text{ee}}^{1,w}[n_\gamma]$. Dependence on the weights enters only via the particle density, $n := \text{Tr}[\hat{\Gamma}^w \hat{n}] = \sum_\kappa w_\kappa n_\kappa$, of the ensemble. Equation (8), and its extension to higher orders in γ discussed later, are the central result of this Letter. In this context, SCE results, analysis, and understanding for ground states [8–11] become special cases of the above more general result.

Proof of Eqs. (8) and (9).—Here, we shall guide the reader through the main steps and key physics. A full proof is reported in Section 1 of the Supplemental Material [38].

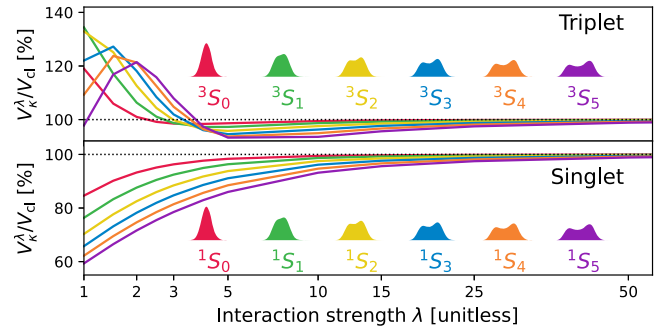


FIG. 1. Ratio of quantum and classical interaction energies for two electrons in a Harmonic well. Six triplet (top) and singlet (bottom) energies are shown. Scaled densities, $4\pi r^2 n(r)$, of the states are also shown for the case $\lambda = 50$.

The salient features can be already grasped by observing the behavior of an interacting system as interactions are increased in a model system. We choose two-electron harmonium in which two electrons interact in an external potential $v_{\text{ext}} = \frac{1}{2} r^2$ with an interaction strength λ . The scaled classical interaction energy of this system is $V_{\text{cl}} = 0.7937 \lambda^{2/3}$ [43]. Quantum solutions may be found numerically. Details are in Supplemental Material Sec. II. Figure 1 shows the interaction energies, $V_\kappa^\lambda := \langle \kappa | \hat{V}_{\text{ee}} | \kappa \rangle$, of six low-lying spherically symmetric triplet (3S) and singlet (1S) states. It is clear that quantum and classical interaction energies all become the same as λ is increased—i.e., all excitations tend toward the same classical limit.

To prove our result for EDFT we need to consider a similar physical setting ($\lambda \rightarrow \infty$), in which instead of fixing the external potential we fix the ensemble density, containing the excited states we want to treat. Proving Eq. (9) then entails showing that the degeneracy behavior carries through to systems in which the density is kept fixed. Our argument involves the expansion of wave functions for large but finite interaction strengths, [9,44] around the strictly correlated limit. In this effectively classical limit, which yields the leading term as $\lambda \rightarrow \infty$ of the ground-state universal functional $F^\lambda[n]$ [10,11], the N -body distribution of an N -electron system is $P_N[n](\mathbf{r}_1, \dots, \mathbf{r}_N) = \int \{[n(\mathbf{s})]/N\} \prod_{i=1}^N \delta(\mathbf{r}_i - \mathbf{f}_i(\mathbf{s})) d\mathbf{s}$ which leads to $F^{\lambda \rightarrow \infty}[n] \rightarrow \lambda V_{\text{ee}}^{\text{SCE}}[n] = \lambda \sum_{i=2}^N \int \{n(\mathbf{r})/[2|\mathbf{r} - \mathbf{f}_i(\mathbf{r})|]\} d\mathbf{r}$. Here, $\mathbf{f}_i(\mathbf{r})$ are co-motion maps that preserve the density and the indistinguishability of electrons [8,12].

At large but finite λ we construct orthonormal wave functions, $|\kappa^\lambda\rangle$, based on quantum harmonic oscillations (QHOs) around the strictly correlated distribution, $P_N[n]$ [9,45]. The QHOs act on curvilinear coordinates orthogonal to the manifold parametrized by the co-motion functions; and contribute at $O(\sqrt{\lambda})$ in the kinetic and potential energies. *Prima facie*, the wave functions $|\kappa^\lambda\rangle$ have different densities. However, it is also possible to

quantize *along* the manifold, which contributes only at $O(1)$ in kinetic energy and is amenable to the Harriman construction [46] of orthogonal orbitals yielding density n . We thereby obtain a countable number of orthonormal wave functions that all have the same density n , and the same energy up to $O(1)$. Thus, $\mathcal{V}_{ee}^{\text{SCE},w}[n] := \sum_{\kappa} w_{\kappa} V_{ee}^{\text{SCE}}[n] = V_{ee}^{\text{SCE}}[n]$ and Eqs. (8) and (9) follow from the equivalence of $\gamma \rightarrow 0^+$ and $\lambda \rightarrow \infty$ in Eq. (3).

Next-leading terms in the low-density limit.—To analyze the next leading terms, it is useful to first rewrite $\mathcal{F}^w[n] := \mathcal{T}^{\text{SCE},w}[n] + V_{ee}^{\text{SCE}}[n]$, taking SCE as the reference system and letting $\mathcal{T}^{\text{SCE},w}$ capture all the ensemble effects. Then an alternative adiabatic connection yields

$$\mathcal{T}^{\text{SCE},w}[n] = \int_1^{\infty} \frac{\mathcal{T}^{\lambda,w}[n]}{\lambda^2} d\lambda. \quad (10)$$

Here, we introduced, $\mathcal{T}^{\lambda,w} = -\lambda^2 \partial_{\lambda}[(\mathcal{F}^{\lambda,w})/\lambda] := \text{Tr}[\hat{T}\hat{\Gamma}^{\lambda,w}]$, where the derivative and trace must be treated with caution, like in Eq. (6). Equation (10) generalizes known results for the ground state-only case [47–49] to the ensembles considered in this Letter.

Next, we show that $\mathcal{T}^{\lambda \rightarrow \infty,w}$ is independent of weights to leading order, which leads to $\mathcal{T}^{\text{SCE},w}[n_{\gamma \rightarrow 0^+}]$ also independent of weights. Ensemblization of known results [9,45,50] gives $\mathcal{T}^{\lambda \rightarrow \infty,w} \rightarrow (\sqrt{\lambda}/2)\mathcal{F}^{\text{ZPE},w}$ where $\mathcal{F}^{\text{ZPE},w}$ involves λ -normalized zero point energy (ZPE) of the QHOs, $|\kappa^{\lambda}\rangle$, introduced earlier. Hence, $\mathcal{T}^{\lambda,w}$ becomes independent of weights if we can show that $\mathcal{F}^{\text{ZPE},w}[n] \equiv \lim_{\lambda \rightarrow \infty} (2/\sqrt{\lambda})\mathcal{T}^{\lambda,w}[n]$ is independent of weights. Supplemental Material Sec. I naturally covers this case—for guidance, below, we touch on essential steps and consequences.

The Harriman construction introduced earlier (also, Supplemental Material Sec. IB) yields $\langle \kappa^{\lambda} | \hat{T} | \kappa^{\lambda} \rangle = \langle 0^{\lambda} | \hat{T} | 0^{\lambda} \rangle + O(1)$ for $\lambda \rightarrow \infty$. Thus, $\mathcal{T}^{\lambda,w} = \sum_{\kappa} w_{\kappa} \langle \kappa^{\lambda} | \hat{T} | \kappa^{\lambda} \rangle = \langle 0^{\lambda} | \hat{T} | 0^{\lambda} \rangle + O(1)$ is independent of weights to leading order, giving weight-independent, $\mathcal{F}^{\text{ZPE},w}[n] \equiv \lim_{\lambda \rightarrow \infty} (2\mathcal{T}^{\lambda,w}[n]/\sqrt{\lambda}) = F^{\text{ZPE}}[n]$. Here, $F^{\text{ZPE}}[n]$ is the well-studied ground state functional [9,44,45], but evaluated on the ensemble density. Using the latter result in (10), and applying scaling laws, finally yields, $\lim_{\gamma \rightarrow 0^+} 2\mathcal{T}^{\text{SCE},w}[n_{\gamma}] = F^{\text{ZPE}}[n_{\gamma}] = \gamma^{3/2} F^{\text{ZPE}}[n]$. Thus we conclude that $\mathcal{T}^{\lambda,w}[n]$ and $\mathcal{T}^{\text{SCE},w}[n]$ are independent of the ensemble weights in the low-density limit. $\mathcal{F}^w[n_{\gamma \rightarrow 0^+}] = \gamma V_{ee}^{\text{SCE}}[n] + \gamma^{3/2} F^{\text{ZPE}}[n]$ is therefore also independent of weights to second leading order. Details of scaling are in Supplemental Material Sec. III.

Where and how does the weight dependence appears in the low-density limit? Equations (S31)–(S37) of Supplemental Material Sec. IB reveal that it appears in the third leading term,

$$\begin{aligned} \mathcal{F}^w[n_{\gamma}] &\xrightarrow{\gamma \rightarrow 0^+} \gamma V_{ee}^{\text{SCE}}[n] + \gamma^{3/2} F^{\text{ZPE}}[n] \\ &\quad + \gamma^2 \Delta \mathcal{T}^{(2),w}[n] + \dots \end{aligned} \quad (11)$$

The $O(\gamma^2)$ term, $\Delta \mathcal{T}^{(2),w} = \sum_{\kappa} w_{\kappa} \Delta T_{\kappa}^{(2)}$, has an explicit weight dependence on each excited state. It captures the energy of oscillations “perpendicular” to the collective ZPE modes, according to the metric dictated by the SCE manifold—see Eq. (S36) and discussion for details. Note, a similar result was previously observed in the special case of Hubbard dimers [51].

Use of high- and low-density limits in approximations.—We have so far derived series expansions in the high-density [Eq. (7)] and low-density [Eq. (11)] limits. Next, we shall illustrate their relevance in applications.

First, we remark that Eqs. (5), (7), and (11) imply that

$$\lim_{\gamma \rightarrow 0^+} \mathcal{E}_{\text{Hxc}}^w[n_{\gamma}] = \gamma \mathcal{E}_{\text{Hx}}^w[n] + \mathcal{E}_{\text{c}}^{\text{GL2},w}[n] + \dots, \quad (12)$$

$$\lim_{\gamma \rightarrow 0^+} \mathcal{E}_{\text{Hxc}}^w[n_{\gamma}] = \gamma V_{ee}^{\text{SCE}}[n] + \gamma^{3/2} F^{\text{ZPE}}[n] + \dots \quad (13)$$

Especially note that the low-density (strictly correlated) limit of both $\mathcal{F}^w[n]$ [see (8)] and $\mathcal{E}_{\text{Hxc}}^w[n]$ depends on the excitation structure only trivially, via the ensemble particle density. Weight dependence appears at higher order.

To illustrate the usefulness of the limits, we first consider the lowest singlet-singlet excitation in dissociating H_2 . This problem is a rather stringent test of density functionals—failed by time-dependent DFT approximations [52,53] because (i) the ground state is dynamically correlated near its minima but becomes strongly correlated when dissociated; (ii) the first excited state is always dynamically correlated, thus cancellation of errors in the approximate excitation energy from the ground state may be unreliable during dissociation; (iii) the first excited state in the KS ensemble involves a superposition of two SDs, and its symmetry and related properties are irreproducible by an adiabatic single-SD approach.

Figure 2 (top) reports the excitation energy $\Delta E_{SS} = E_{S_1} - E_{S_0}$ of the lowest singlet states (S_0 and S_1) of H_2 using: exact exchange (EXX) energies—the leading term in the *high*-density series of Eq. (12); Görling-Levy [34] (GL2) perturbation theory (renormalized to avoid numerical singularities)—the next leading term of (12); and the interaction strength interpolation (ISI) approximation [54,55] that uses high- and low-density limits—the latter via the harmonium point charge plus continuum (HPC) approximation [55]. Note, all approximations are *ensemblized* versions of ground state analogs, i.e., $E_{\text{Hxc}}^{\text{approx}} \rightarrow \mathcal{E}_{\text{Hxc}}^{\text{approx},w}$ is adapted for excited states. All relevant energy expressions and technical details on the calculations are in Supplemental Material Sec. IV.

Only ISI performs well across the whole H_2 dissociation curve, which unambiguously highlights the benefit of using

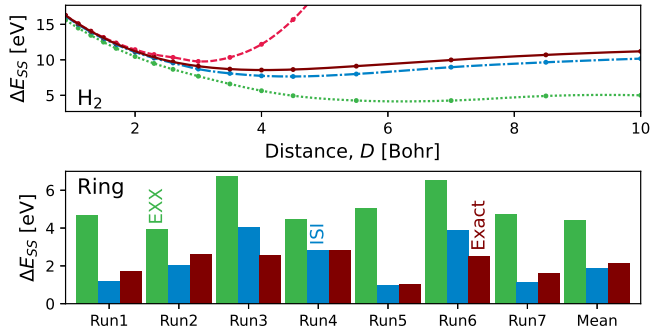


FIG. 2. Excitation energies, for dissociating H_2 (top); and seven random runs and the mean of 25 runs for a ring of wells with disorder (bottom). Ensembled EXX [dotted line (green)], GL2 [dashed line (red)], ISI [dash-dotted line (blue)], and exact [solid lines (maroon)] energies are shown. GL2 errors in the ring are so large they cannot be shown in the lower panel.

both Eq. (12) and Eq. (13) to construct approximations that capture different correlation regimes. In fact, using only Eq. (12) leads to very poor results for the ground state energy: EXX overestimates and GL2 drastically underestimates as correlations become stronger.

Next, we carry out similar calculations for four electrons in a ring of four quantum wells; see Supplemental Material Sec. IV for further details. Lattice disorder in this system yields $\Delta E_{SS} = 2.15$ eV on average, versus $\Delta E_{SS} = 0.003$ eV of the ordered lattice. Results are shown in Fig. 2 (bottom). Again, we see that the low-density behavior included in ISI reduces errors: from 100% (EXX) down to 12% (ISI). GL2 energies (not shown) have orders of magnitude worse errors. This example (also, Ref. [56]) thus suggests that seamless interpolation between high- and low-density limits may be crucial for predicting optical gaps in disordered nanostructures.

Summary and conclusions.—The results presented in this Letter describe, via ensemble density functionals, the behavior of excited many-electron states in the paradigmatic high-density (weakly correlated) and low-density (strictly correlated) limits (regimes)—summarized for the important \mathcal{E}_{Hxc} functional in Eqs. (12) and (13), respectively.

The high-density limit follows intuition and connects directly to previous results which use the *ensemble* Kohn-Sham system as a reference system. The corresponding auxiliary pure states have the form of symmetry adapted combination of Slater determinants; and \mathcal{E}_{Hxc} has strong weight dependence. Approximations based on this limit have already successfully described weakly to moderately correlated excitations.

The low-density limit, in contrast, revealed an unexpected fact: the first two leading order terms of excited states may be described by existing tools used for strictly correlated *ground* states. Therefore the ensemblization of ground-state approximations is, for once, straightforward.

Dependence of \mathcal{E}_{Hxc} on the weights (and therefore excitation structure) only shows up in the third leading order term. The provided model applications illustrate that generally correlated regimes of excited states require seamless treatment of both density regimes.

One immediate consequence of the present Letter is that electronic interaction models must interpolate between Fermionic mean-field-like excitation-structure dependence at high densities, and no excitation-structure dependence at low densities. Not only is this of direct importance for traditional analytic-driven approximations, as seen in the examples reported here, it also provides constraints for data-driven methodologies based on machine learning. Ensemble-derived constraints were used to great success in the machine-learned “Deep Mind 21” ground state approximation [57]—our Letter promises to extend this success to excited states to provide complements or alternatives to existing finite order (see examples above) or infinite order (via Green’s functions) many-body perturbation theory.

Natural next steps from the present results are to consider extended systems with uncountable excitations, finite-temperature ensembles, and magnetic interactions. Finite temperature imposes a λ dependence on the weights. Prior work [25,58] showed that the high (low)-density limit may be more relevant to the behavior of density functionals at low (high) temperature. Magnetic interactions require extra basic densities (e.g., spin densities and currents) and related Hxc quantities; [59,60] and must consistently fulfill gauge symmetries [61]. Further work along both lines is being pursued.

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